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A "sodium trap" based on benzo-15-crown-5 with an exocyclic *N*-(thiophosphoryl)thiourea moiety

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Abstract

For *N*-(thio)phosphorylthioureas of the common formula RC(S)NHP(X)(O*i*Pr)$_2$ $\mathbf{HL^I}$ (R = *N*-(4′-aminobenzo-15-crown-5), X = S), $\mathbf{HL^{II}}$ (R = *N*-(4′-aminobenzo-15-crown-5), X = O), $\mathbf{HL^{III}}$ (R = PhNH, X = S), $\mathbf{HL^{IV}}$ (R = PhNH, X = O), and (*N*,*N*′-bis-[C(S)NHP(S)(O*i*Pr)$_2$]$_2$-1,10-diaza-18-crown-6) $\mathbf{H_2L^V}$, salts $\mathbf{LiL^{I,III,IV}}$, $\mathbf{NaL^{I–IV}}$, $\mathbf{KL^{I–IV}}$ $\mathbf{M_2L^V}$ (M = Li^+, Na^+, K^+), $\mathbf{Ba(L^{I,III,IV})_2}$, and $\mathbf{BaL^V}$ have been synthesized and investigated. Compounds $\mathbf{NaL^{I,II}}$ quantitatively drop out as a deposit in ethanol medium, allowing the separation of Na^+ and K^+ cations. This effect is not displayed for the other compounds. The crystal structures of $\mathbf{HL^{III}}$ and the solvate of the composition [$\mathbf{K(Me_2CO)L^{III}}$] have been investigated by X-ray crystallography.

Keywords: Chelates; Coordination modes; Crown-ethers; Crystal structures; *N*-thioacylamido(thio)phosphates

1. Introduction

Crown-ethers and azamacrocycles modified by exocyclic groups are widely applied as complexing agents, selective to cations of alkaline, earth-alkaline, and d-metals [1,2], lanthanides and actinides [3], and Tl(I) [4]. However, in the literature there is no data about direct (not-extraction) highly effective separation of alkaline metal cations using crown compounds.

On the formation of complexes of alkaline metal salts [M^+A^-] with crown-ethers, as a rule, there is an increase in solubility of the formed adduct [M(crown)]$^+A^-$ in an organic phase [5]. However, a combination of crown-ether and negative charged chelating units in a ligand molecule can lead to interesting cooperative effects.

Herein we present data about the structures and properties of *N*-(thio)phosphorylthioureas of the common formula RC(S)NHP(X)(O*i*Pr)$_2$, ($\mathbf{HL^{I–IV}}$) and *N*,*N*′-bis-[C(S)NHP(S)(O*i*Pr)$_2$]$_2$-1,10-diaza-18-crown-6 ($\mathbf{H_2L^V}$) (Scheme 1), and their salts with Li^+, Na^+, K^+, Ba^{2+}.

It is known [6] that *N*-(thio)phosphorylthioureas in aqueous alcohol medium are weak acids: $\mathbf{HL^{III}}$ p*K* 8.1 (96% aq. EtOH) [7], 8.28 (96% aq. *i*PrOH) [8]; $\mathbf{HL^{IV}}$ p*K* 6.93 (96% aq. *i*PrOH) [8]; $\mathbf{H_2L^V}$ pK_1 = 9.2, pK_2 = 10.2 (96% aq. EtOH) [7]. These compounds are able to form salts with cations of alkaline metals. There is no information on the crystal structures of salts of *N*-(thio)phosphorylthioureas in the literature. However, the structures of some close analogues of these compounds – salts of *N*-(thio) phosphorylamides and thioamides, containing the fragment C(X)NHP(Y)R′$_2$ (X, Y = O, S), have already been investigated. Compounds of the formula [M(CCl$_3$C(O)NP(O)(OMe)$_2$)] as crystals form dimers (M = Na^+) or polymeric chains M = Rb^+ [9]. Potassium salts of thioamides

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